

PATENT COOPERATION TREATY

PCT


INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference PA135755/PCT		FOR FURTHER ACTION	See Form PCT/PEA/416
International application No. PCT/IB2004/000654	International filing date (day/month/year) 10.03.2004	Priority date (day/month/year) 10.03.2003	
International Patent Classification (IPC) or national classification and IPC C07C7/10, C10G21/16			
Applicant SASOL TECHNOLOGY (PROPRIETARY) LIMITED et al			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 4 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 06.01.2005		Date of completion of this report 13.06.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized Officer O'Sullivan, P Telephone No. +31 70 340-4511	



**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/IB2004/000654

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1, 2, 4-14 as originally filed
3 received on 06.05.2005 with letter of 06.05.2005

Claims, Numbers

1-18 received on 06.05.2005 with letter of 06.05.2005

Drawings, Figures

1-3 as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/IB2004/000654

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-18
	No: Claims	
Inventive step (IS)	Yes: Claims	1-18
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-18
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

D1: WO 02/31085 A
D2: US-A-4 603 225
D3: DE 199 11 910 A
D4: US-A-4 686 317

1. Novelty (Art 33(2) PCT)

1.1 D1 discloses a process for separating olefins and paraffins from oxygenates in a liquid hydrocarbon stream (see page 3, paragraph 1- page 4, paragraph 4). The hydrocarbon, which originates from a Fischer-Tropsch process, is first distilled to give, for example, a C₄ to C₁₈ hydrocarbon. The oxygenates are separated therefrom by extraction with a polar solvent which comprises a mixture of water and an organic liquid such as, but not limited to, propanol. The water typically comprises no more than the azeotropic composition of water in the organic liquid. There is no mention of the polar organic solvent and water being added separately. Present claims 1-18 can therefore be considered novel over D1.

1.2 D2 discloses (claim 1 and 5) a process for separating dimethyl ether from a hydrocarbon mixture which comprises contacting said hydrocarbon mixture with an aqueous solution containing a polar oxygenated hydrocarbon, preferably methanol. There is however no mention of the methanol and water being added separately. Present claims 1-18 can therefore be considered novel over D2.

1.3 D3 (column 1, lines 1-25) discloses the liquid-liquid extraction of oxygenates from a hydrocarbon stream. The solvent chosen is a solution of either methanol, ethanol, propanol or butanol in water. There is however no mention of the alcohol and water being added separately. Present claims 1-18 can therefore be considered novel over D3.

2. Inventive Step (Art 33(3) PCT)

2.1 The difference between the subject-matter of D1 and the present claim 1 is that there is no mention of methanol and water being added separately in the latter. Comparative example 1 and example 2 of the present application demonstrate that adding the water and methanol separately leads to an improved olefin/paraffin recovery while the olefin/paraffin ratio was left unchanged. Therefore the problem to be solved may be formulated as the provision of a process for the removal of oxygenates from a hydrocarbon stream whereby the olefin/paraffin recovery rate is improved. The solution is not considered obvious as the skilled man is not aware of any teaching D1 nor any inherent common knowledge he may possess which would lead him to carry out this adjustment in order to solve the problem in hand. Therefore, adding methanol and water separately in said process is considered inventive. Claims 1-18 are therefore considered inventive.

2.2 The same reasoning applies to D2 and D3 as to D1, above.

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SUMMARY OF THE INVENTION

According to the invention there is provided a commercially viable process for extracting oxygenates from a hydrocarbon stream, typically a fraction of the condensation product of a Fischer-Tropsch reaction, while preserving the olefin content of the condensation product.

The oxygenate extraction process is a liquid-liquid extraction process that preferably takes place in an extraction column using methanol and water as the solvent, wherein the methanol and water are added separately to the extraction column.

The hydrocarbon stream is fed into the extraction column at, or near, the bottom thereof, a methanol stream is fed into the extraction column at, or near, the top thereof, and a water stream is fed into the extraction column between the hydrocarbon stream and methanol stream.

An extract from the liquid-liquid extraction may be sent to a solvent recovery column from which a tops product comprising polar organic solvent, olefins and paraffins is recycled to the extraction column, thereby enhancing the overall recovery of olefins and paraffins. A bottoms product from solvent recovery column may also be recycled to the extraction column.

A raffinate stream from the extraction column is preferably sent to a stripper column from which a hydrocarbon stream containing more than 90% by weight olefins and paraffins and typically less than 0.2% by weight, preferably less than 0.02% by weight, most preferably less than 0.01% by weight oxygenates exits as a bottoms product. The recovery of olefins and paraffins over the oxygenate extraction process is preferably greater than 70%, more preferably greater than 80%, while the olefin/paraffin ratio is at least substantially preserved.

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CLAIMS

1. A process of extracting oxygenates from a hydrocarbon stream using an extraction solvent comprising methanol and water, wherein the methanol and water are added separately in the extraction process.
2. The process according to claim 1, wherein the hydrocarbon stream is the fractionated hydrocarbon condensation product of a Fischer-Tropsch reaction.
3. The process according to claim 2, wherein the hydrocarbon stream is the fractionated hydrocarbon condensation product of a low temperature Fischer-Tropsch reaction.
4. The process according to claim 3, wherein, prior to extraction, the hydrocarbon condensation product contains 15% to 30% by weight olefins and 5% to 15% by weight oxygenates.
5. The process according to claim 1, wherein the liquid-liquid extraction takes place in a liquid extraction column and the methanol and water are added separately to the column.
6. The process according to claim 5, wherein the hydrocarbon stream is fed into the extraction column at, or near, the bottom thereof, a methanol stream is fed into the extraction column at, or near, the top thereof, and a water stream is fed into the extraction column between the hydrocarbon stream and methanol stream.
7. The process according to claim 6, wherein a raffinate from the extraction column is sent to a raffinate stripper column from which a hydrocarbon feed stream containing olefins and paraffins and less than 0.2% by weight oxygenates exits as a bottoms product.

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8. The process according to claim 7, wherein a raffinate from the extraction column is sent to a raffinate stripper column from which a hydrocarbon feed stream containing olefins and paraffins and less than 0.02% by weight oxygenates exits as a bottoms product.
9. The process according to claim 8, wherein a raffinate from the extraction column is sent to a raffinate stripper column from which a hydrocarbon feed stream containing olefins and paraffins and less than 0.01% by weight oxygenates exits as a bottoms product.
10. The process according to claim 1, wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction step, thereby enhancing the overall recovery of olefins and paraffins.
11. The process according to claim 10, wherein the aqueous phase of a bottoms product from the solvent recovery column is recycled to the extraction step.
12. The process according to claim 11, wherein the extraction solvent has a water content of more than 3% by weight.
13. The process according to claim 12, wherein the extraction solvent has a water content of about 5% - 15% by weight.
14. The process according to claim 12 or claim 13, wherein the hydrocarbon stream is fractionated in the C₈ to C₁₆ range.
15. The process according to claim 14, wherein the hydrocarbon stream is fractionated in the C₁₀ to C₁₉ range.

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16. The process according to any one of the preceding claims, wherein the recovery of olefins and paraffins over the oxygenate extraction process is greater than 70%.
17. The process according to claim 16, wherein the recovery of olefins and paraffins over the oxygenate extraction process is greater than 80%.
18. The process according to any one of the preceding claims, wherein the olefin/paraffin ratio in the hydrocarbon stream over the oxygenate extraction process is substantially preserved.